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(54)【発明の名称】　非水系電解質二次電池用正極活物質および該正極活物質を用いた非水系電解質二次電池

(57)【要約】
【課題】　高負荷時における放電容量が優れた非水系電解液二次電池用正極活物質および該正極活物質を用いた非水系電解質二次電池を提供する。
【解決手段】　実質的に一般式ＬｉＣｏＯ$_2$で表されるコバルト酸リチウムの微小一次粒子が多数凝集した二次粒子からなり、かつ該二次粒子には電解液が浸透し得る微小な隙間を多数有し、かつタップ密度が２．２ｇ／ｃｍ^{3}以上であるコバルト酸リチウムを用いた非水系電解質二次電池用正極活物質であって、前記微小一次粒子の少なくとも一部が二次粒子の中心から外方に向かって放射状に並び、かつ放射状に並んだ微小一次粒子と隣接する同じく放射状に並んだ微小一次粒子との間に隙間を有し、また前記二次粒子を構成している微小一次粒子の相互の少なくとも一部が焼結により接合していることが好ましく、また該二次粒子の形状が球状あるいは楕円球状であることが好ましい。そしてこのような正極活物質を用いた非水系電解質二次電池を特徴とする。

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【特許請求の範囲】

【請求項１】　実質的に一般式ＬｉＣｏＯ$_2$で表されるコバルト酸リチウムの微小一次粒子が多数凝集した二次粒子からなり、かつ該二次粒子には電解液が浸透し得る微小な隙間を多数有し、さらにタップ密度が２．２ｇ／ｃｍ^{3}以上であるコバルト酸リチウムを用いた非水系電解質二次電池用正極活物質であって、前記微小一次粒子の少なくとも一部が二次粒子の中心から外方に向かって放射状に並び、かつ放射状に並んだ微小一次粒子と隣接する同じく放射状に並んだ微小一次粒子との間に隙間を有することを特徴とする非水系電解質二次電池用正極活物質。

【請求項２】　前記二次粒子を構成している微小一次粒子の相互の少なくとも一部が焼結により接合していることを特徴とする請求項１記載の非水系電解質二次電池用正極活物質。

【請求項３】　前記二次粒子の形状が球状あるいは楕円球状であることを特徴とする請求項１または２記載の非水系電解質二次電池用正極活物質。

【請求項４】　前記二次粒子の平均粒径が２μｍ以上で３０μｍ以下であることを特徴とする請求項１～３のいずれか１項記載の非水系電解質二次電池用正極活物質。

【請求項５】　前記一次粒子の平均粒径が０．４μｍ以上で１０μｍ以下であることを特徴とする請求項１～４のいずれか１項記載の非水電解質二次電池用正極活物質。

【請求項６】　請求項１～５のいずれか１項記載の正極活物質を構成要素とすることを特徴とする非水系電解質二次電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は負極にリチウム金属、リチウム合金あるいはリチウムを吸蔵できる炭素などを用いる非水系電解質二次電池の正極活物質に関するものであり、特に電池の高負荷時の放電容量を向上した非水系電解質二次電池用正極活物質および該正極活物質を用いた非水系電解質二次電池に関するものである。

【０００２】

【従来の技術】近年、携帯電話やノート型パソコンなどの携帯機器の普及に伴い、小型、軽量で、かつ高いエネルギー密度を有する高い容量を持つ二次電池の開発が強く望まれている。このようなものとしてリチウム金属、リチウム合金あるいは炭素を負極として用いるリチウムイオン二次電池があり、現在研究開発が盛んに行われている。そして合成が比較的容易なコバルト酸リチウム（ＬｉＣｏＯ$_2$）を正極活物質に用いたリチウムイオン二次電池は、４Ｖ級の高い電圧が得られるため、高エネルギー密度を持つ電池として期待され、広く実用化されている。

【０００３】しかし、最近のさらなる高容量化や大電流

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化の要求に対して正極活物質のタップ密度を上げることや、正極活物質と混合する炭素などの導電剤量を減らして実質的に正極活物質を増やすなどの対策が必要となってきた。

【０００４】

【発明が解決しようとする課題】通常ＬｉＣｏＯ$_2$は、例えば炭酸リチウムのようなリチウム塩と、例えば炭酸コバルトのようなコバルト化合物とを所定量混合し、６００℃～１１００℃までの温度で焼成したり（特開平１－３０４６６４号公報）、または炭酸リチウムと平均粒径が２μｍ～２５μｍの四三酸化コバルトを所定量混合して８００℃～９００℃で焼成する（特開平９－２８３１４４号公報）ことにより得られものである。

【０００５】しかしながら、従来のＬｉＣｏＯ$_2$では充填密度が上がらなかったり、導電剤の量を減らすと放電容量や高負荷時の容量が低下するなどの問題があった。このような問題を解決するためにコバルト酸リチウムの微小結晶が多数凝集して球状ないし楕円球状の二次粒子からなる非水系電解質二次電池用正極活物質が提案されている（Ａｂｓｔｒａｃｔｓ　ｏｆ　９ｔｈ　Ｉｎｔｅｒｎａｔｉｏｎａｌ　Ｍｅｅｔｉｎｇ　ｏｎ　Ｌｉｔｈｉｕｍ　Ｂａｔｔｅｒｉｅｓ，Ｐｏｓｔｅｒ　ＩＩ　Ｔｈｕｒ５６，１９９８）。

【０００６】確かに前記した正極活物質はタップ密度が高く、通常の負荷時における放電容量が高い優れた材料ではあるものの、高負荷時における放電容量の改善は未だ十分ではなかった。

【０００７】本発明は上記した従来の正極活物質に関する問題点の解決を図るものであり、その目的とするところは、高負荷時における放電容量が優れた非水系電解液二次電池用正極活物質および該正極活物質を用いた非水系電解質二次電池を提供することである。

【０００８】

【課題を解決するための手段】本発明者らは高負荷時の容量が不十分である原因として、二次粒子を構成している一次粒子同士が互いに密に接合して充電放電時において電解液が十分に二次粒子内部に浸透せず、その結果リチウムイオンが高負荷時における電流に十分追随できなくなり容量が向上しないという点に着目して、正極活物質の一次粒子の大きさ、形状、また微小一次粒子が集合した二次粒子の大きさ、形状、一次粒子間の隙間などについてさらに鋭意検討を行った結果、これらの因子を制御することにより高容量で、かつ高負荷時の放電容量が良好な正極活物質が得られることを見出し本発明を完成するに至った。

【０００９】すなわち本発明の第１の実施態様に係る非水系電解質二次電池用正極活物質は、実質的に一般式ＬｉＣｏＯ$_2$で表されるコバルト酸リチウムの微小一次粒子が多数凝集した二次粒子からなり、かつ該二次粒子には電解液が浸透し得る微小な隙間を多数有し、かつタッ

プ密度が２．２ｇ／ｃｍ^{3}以上であるコバルト酸リチウムを用いた非水系電解質二次電池用正極活物質であって、前記微小一次粒子の少なくとも一部が二次粒子の中心から外方に向かって放射状に並び、かつ放射状に並んだ微小一次粒子と隣接する同じく放射状に並んだ微小一次粒子との間に隙間を有することを特徴とするものである。そして前記二次粒子を構成している微小一次粒子の相互の少なくとも一部が焼結により接合していることが好ましく、また該二次粒子の形状が球状あるいは楕円球状であることが好ましい。さらに前記二次粒子の平均粒径が２μｍ以上で３０μｍ以下であり、また該一次粒子の平均粒径は０．４μｍ以上で１０μｍ以下であることが好ましい。なおコバルトの４０モル％以下をコバルト以外の金属で置換したものでも同様な効果を得ることができる。

【００１０】つぎに本発明の第２の実施態様に係る非水系電解質二次電池は、前記第１の実施態様に係る正極活物質を構成要素としたことを特徴とするものである。

【００１１】

【発明の実施の形態】本発明に係る非水系電解質二次電池用の正極活物質によれば、二次粒子を構成している一次粒子の少なくとも一部が二次粒子の中心から外方に向かって放射状に並び、かつ放射状に並んだ微小結晶と隣接する同じく放射状に並んだ微小一次粒子との間に隙間を有するよう構成されているので、電解液が効率よく二次粒子の内部に浸透して二次粒子内部の正極活物質の微小一次粒子と十分接触するため、高負荷時における放電特性を良好なものとすることができる。

【００１２】そして本発明において微小一次粒子の平均粒径を０．４μｍ～１０μｍの範囲とした理由は、０．４μｍ未満では電解液の分解反応が促進され、二次電池の安全性に支障が出てくるからであり、一方１０μｍを超えると高負荷時の放電容量が低下するからである。さらに二次粒子の平均粒径を２μｍ～３０μｍとした理由は、２μｍ未満ではタップ密度が上がらず、また導電性を付与するために必要な導電剤の量が増加してしまい、一方二次粒子の平均粒径が３０μｍを超えると電極を作製する時に塗布性が劣るなどの問題が生じるからである。

【００１３】また前記微小一次粒子自体は微粒であるが、それら相互が少なくとも一部焼結で接合して平均粒径が２μｍ～３０μｍの範囲内にある球状あるいは楕円球状の二次粒子で正極活物質を形成することが好ましい。微小一次粒子相互が少なくとも一部焼結により接合した球状あるいは楕円球状の二次粒子とした理由は、これにより電気的伝導性を向上させることができ、必要な導電剤の量を減らして充填密度を向上させることが可能となるためである。

【００１４】二次粒子の形状を球状あるいは楕円球状とした理由は、これら以外の不定形の形状とした場合、２．２ｇ／ｃｍ^{3}以上のタップ密度を得られず、かつ放電容量が劣るからである。

【００１５】

【実施例】以下本発明を実施例および比較例とともに詳細に説明する。なお以下の実施例および比較例で得られた正極活物質のタップ密度はいずれも２．２ｇ／ｃｍ^{3}以上であったので、個別には特に言及しない。

【００１６】［実施例］二次粒子がほぼ球状で平均粒径が２μｍ～３０μｍである塩基性炭酸コバルトと炭酸リチウムを所定量混合した後、空気中９００℃で１０時間焼成してコバルト酸リチウムの二次粒子を得た。

【００１７】得られた粒子の中から少量を抜き取り、走査型電子顕微鏡（ＳＥＭ）で二次粒子の表面を５０００倍で観察したところ、平均粒径が０．４μｍ～５μｍ程度の一次粒子が多数凝集したほぼ球状の二次粒子となっていた。さらにこの二次粒子には図１のＳＥＭ写真に示すような０．２μｍ～２μｍ程度の多数の空隙が認められた。

【００１８】つぎにＳＥＭの倍率を１５０００倍にして観察したところ、二次粒子を構成している一次粒子の相互はそれぞれ一部が焼結により接合していることが確認できた。そして少量のコバルト酸リチウムの二次粒子をエポキシ樹脂に埋め込んだ後、ダイヤモンドカッターを有するミクロトーム切断機で二次粒子を切断し、二次粒子断面を露出させた。露出した断面を前記と同様にＳＥＭにて２０００倍で観察したところ、図２のＳＥＭ写真に示すように二次粒子を構成している微小一次粒子が放射状に並び、かつ隣接する同じく放射状に並んだ微小一次粒子との間に隙間を有する組織を確認することができた。

【００１９】得られたコバルト酸リチウム二次粒子の高負荷時の放電容量の測定は内田らの報告（電気化学、Ｖｏｌ．６５、９５４（１９９７））に基づいた単一粒子の電気化学測定装置で行った。この測定装置を使用すると導電剤やバインダーなどの影響を受けずに二次粒子単独の評価が可能となる。前記測定装置は図３に示すように、ガラスフィルターで上下に仕切られた二室型のセルを用いて、コバルト酸リチウムの二次粒子１をガラスフィルタ５上に載置し、セルを光学顕微鏡２の観察台にセットする。該光学顕微鏡に取りつけたＣＣＤカメラの映像で二次粒子１を確認しながら、マイクロマニピュレータ４に取り付けたマイクロリード電極３（直径２５μｍのＰｔ／Ｒｈ細線）の先端を粒子１に接触させた。

【００２０】一方電解液６には１Ｍ－ＬｉＣｌＯ$_4$／エチレンカーボネート（ＥＣ）－ジーエチルカーボネート（ＤＥＣ）（１：１）混合溶液を、また対極７にはリチウム金属を用いた。この測定装置は大気中からの水分の混入を防ぐため、露点－６０℃の乾燥空気を流したドライボックスで行った。微小電流用ポンテショスタット８を用いて、充電時は１時間でリチウム金属の対極７に対

するマイクロリード電極３の電位が４．３Ｖになるように一定電流を流して、その電流値を測定している二次粒子の１Ｃとした。放電は所定の一定電流値で対極７に対するマイクロリード電極３の電位が３．０Ｖになるまで流し、その時流れた電気量を放電容量とした。所定の電流値は充電時の電流値を基準として、例えば５倍なら５Ｃ、１０倍なら１０Ｃなどとした。

【００２１】そして図４に本発明の実施例により得られた正極活物質の単独二次粒子の充放電プロファイル例を示し、図４（ａ）は充電１Ｃ、放電１０Ｃ、図４（ｂ）は充電１Ｃ、放電２０Ｃで得られた充放電プロファイル例である。図４より分る通り本発明の実施例によれば放電２０Ｃの高負荷においても過電圧は非常に小さく放電特性は良好であった。

【００２２】［比較例］二次粒子がほぼ球状で平均粒径が２～３０μｍである塩基性炭酸コバルトを予め空気中で８５０℃、４時間で加熱した後、所定量の炭酸リチウムと混合し、空気中９００℃で１０時間焼成してコバルト酸リチウムの二次粒子を得た。

【００２３】得られた粒子の中から少量を抜き取り、ＳＥＭで二次粒子の表面を５０００倍で観察したところ、平均粒径が０．４μｍ～５μｍ程度の一次粒子が多数凝集したほぼ球状の二次粒子となっていた。さらにこの二次粒子には図５のＳＥＭ写真に示すような０．２μｍ～２μｍ程度の多数の空隙が認められた。

【００２４】つぎにＳＥＭの倍率を１５０００倍にして観察したところ、二次粒子を構成している一次粒子の相互はそれぞれ一部が焼結により接合していることが確認できた。さらに少量の二次粒子をエポキシ樹脂に埋め込んだ後、ダイヤモンドカッターを有するミクロトーム切断機で二次粒子を切断し、二次粒子断面を露出させた。露出した断面を前記と同様にＳＥＭにて２５００倍で観察したところ、図６のＳＥＭ写真に示すように二次粒子を構成している微小一次粒子の間に隙間が認められたが、前記した実施例のような放射状の組織は存在しなかった。

【００２５】得られたコバルト酸リチウム二次粒子の高負荷特性を実施例と同様な方法で測定した。図７に比較例により得られた正極活物質の単独二次粒子の充電１Ｃ、放電１０Ｃで得られた充放電プロファイルを示すが、１０Ｃの放電においても非常に大きな過電圧が観察された。

【００２６】なお本発明における非水系電解質二次電池用正極活物質はリチウムとコバルトを主成分とした実質的に$LiCoO_2$からなるが、結晶の安定性や、電気伝導性あるいは製造価格の低下を目的として他の金属でＣｏの一部を置換した材料、具体的にはＣｏの４０モル％以下をＮｉ、Ｍｎ、Ａｌ、Ｚｎ、Ｍｇ、Ｃａ、Ｔｉ、Ｆｅ、Ｓｎの中から選ばれた１種あるいは２種以上の金属で置換した正極活物質でも本発明の形態を採れば高負荷特性を改善する効果が実現できる。

【００２７】以上の実施例と比較例から明らかなように、本発明に係る非水系電解質二次電池用正極活物質は平均粒径が０．４μｍ～１０μｍの範囲にある一次粒子が多数凝集して平均粒径が２μｍ～３０μｍの範囲にあるほぼ球状の二次粒子からなり、かつ二次粒子を構成している微小一次粒子の少なくとも一部が二次粒子の中心から外方に向かって放射状に並び、かつ放射状に並んだ微小一次粒子と隣接する同じく放射状に並んだ微小一次粒子との間に隙間を有しているものであることから、電解液が効率よく二次粒子内部に浸透して一次粒子の隅々にまで行渡るため、高負荷時においても過電圧が小さく放電特性が大きく向上したものである。

【００２８】これに対して、比較例のように二次粒子内部の一次粒子の並び方が不規則であったり、隙間が粒子により遮断されているような構造では、高負荷時に大きな過電圧が認められた。この原因は定かではないが、電解液が内部に浸透する時に大きな抵抗となり高負荷時における過電圧が大きくなったものと思慮される。

【００２９】また本発明における非水系電解質二次電池用正極活物質の二次粒子は平均粒径が４μｍ～３０μｍのほぼ球状（ないしはほぼ楕円球状）であることから、タップ密度も高く、また電極作製時の塗布性にも優れ、さらに一次粒子が互いに一部焼結しているので、一次粒子間の電気抵抗が低く、また電極を作製する際に二次粒子が潰れることがないので、集電体から一次粒子が脱落したりすることもない。またこのコバルト酸リチウムを正極活物質として用いて作製した非水系電解質二次電池は高負荷時における放電特性に優れていた。

【００３０】

【発明の効果】以上述べた通り本発明に係る非水系電解質二次電池用正極活物質およびこれを用いた二次電池は放電容量、高負荷特性を向上させることが可能となり、これにより優れた非水系電解質二次電池を提供することが可能となる。

【図面の簡単な説明】

【図１】実施例で得られたコバルト酸リチウム二次粒子の走査型電子顕微鏡（×５０００）による粒子構造の写真である。

【図２】実施例で得られたコバルト酸リチウム二次粒子の断面の走査型電子顕微鏡（×２０００）による粒子構造の写真である。

【図３】二次粒子単独の高負荷特性を測定する装置の概略図である。

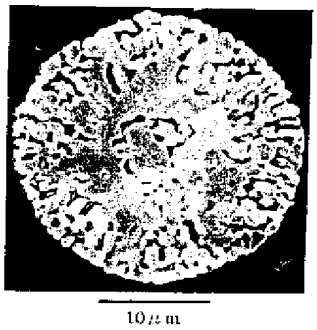
【図４】実施例で得られた正極活物質の単独二次粒子の充放電プロファイルを示すグラフで、（ａ）は充電１Ｃ、放電１０Ｃ、（ｂ）は充電１Ｃ、放電２０Ｃで得られた充放電プロファイル例である。

【図５】比較例で得られたコバルト酸リチウム二次粒子の走査型電子顕微鏡（×５０００）による粒子構造の写

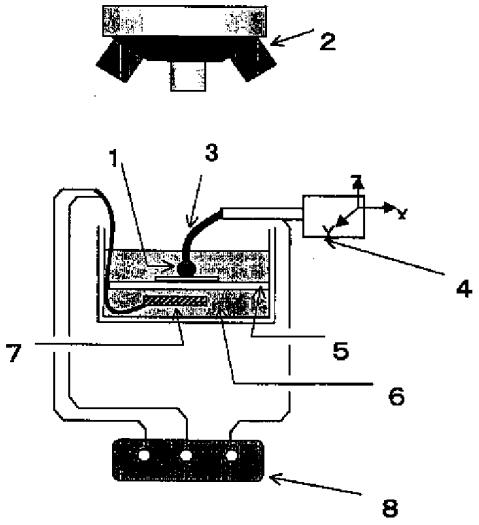
真である。
【図６】比較例で得られたコバルト酸リチウム二次粒子の断面の走査型電子顕微鏡（×２５００）による粒子構造の写真である。
【図７】比較例で得られた正極活物質の単独二次粒子の充放電プロファイルを示すグラフである。
【符号の説明】
１　単一正極活物質二次粒子
２　顕微鏡
３　マイクロリード電極
４　マイクロマニピュレータ
５　ガラスフィルタ
６　電解液
７　対極
８　微小電流ポテンショスタット

【図１】

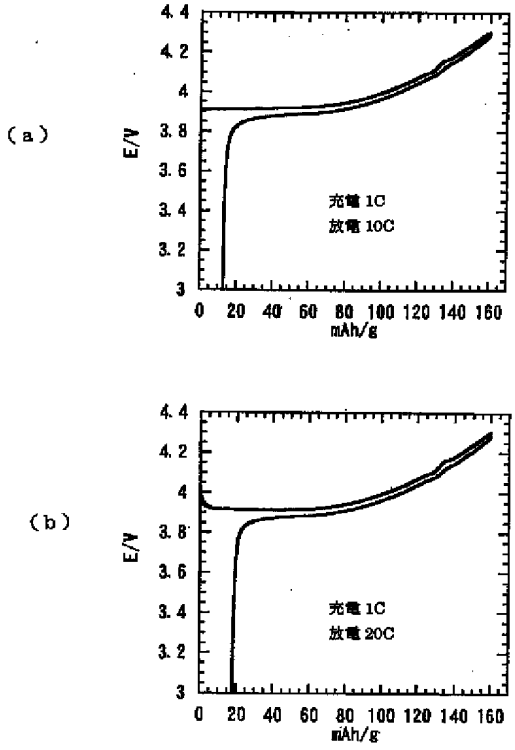
【図２】



【図３】



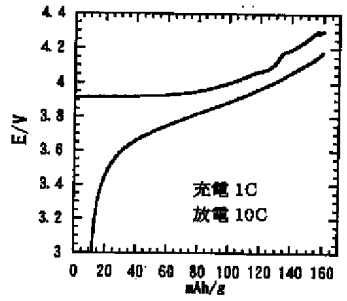
【図４】



【図５】

【図６】

【図７】



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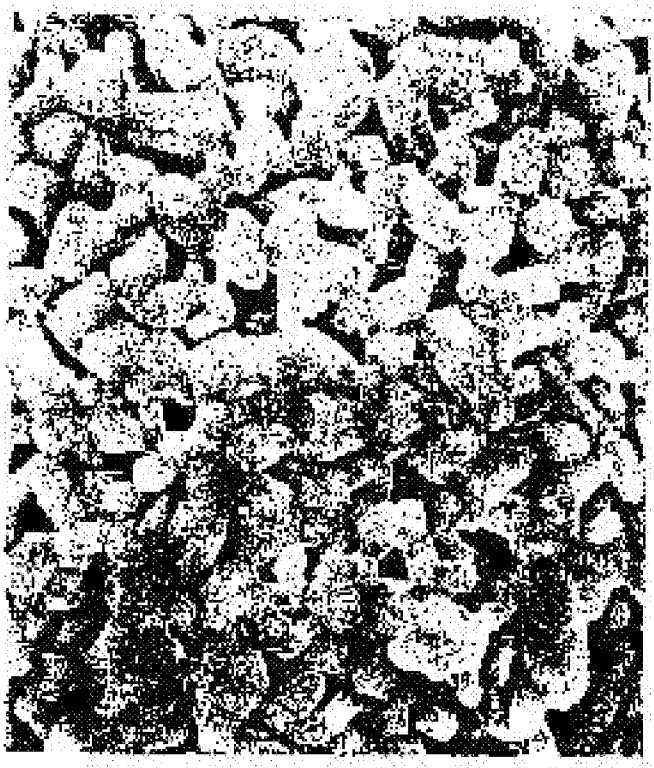
SOMA MASANORI

(54) POSITIVE ELECTRODE ACTIVE MATERIAL FOR NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY AND BATTERY USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a positive electrode active material for a non-aqueous electrolyte secondary battery and a non-aqueous electrolyte secondary battery using the same which is excellent in discharge capacity at a high load.

SOLUTION: This is a positive electrode active material for non-aqueous electrolyte secondary battery, which is comprised of secondary particles of fine primary particles of lithium cobalt oxide as expressed in substance in the general formula LiCoO2 having coagulated in many quantity and, in which the secondary particles have many fine gaps where the electrolyte can infiltrate, and further in which the lithium cobalt oxide having a tap density of 2.2 g/cm3 or more is used. And it is desirable that at least a part of the above fine primary particles are arranged in radiation toward outside from the center of the secondary particles, and that there exists a gap between the fine primary particles also arranged in radiation adjoining the fine primary particles and the above fine primary particles in



radiation, and further, that at least a part of the fine primary particles mutually composing the above secondary particles are connected each other by sintering. And also it is desirable that the configurations of the secondary particles are spherical or elliptic spheroidal.

* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1]It consists of an aggregated particle which many minute primary particles of cobalt acid lithium substantially expressed with general formula $LiCoO_2$ condensed, And it is the positive active material for nonaqueous electrolyte secondary cells using cobalt acid lithium whose tap density it has many minute crevices in which an electrolysis solution may permeate this aggregated particle, and is more than 2.2 g/cm^3 further, Positive active material for nonaqueous electrolyte secondary cells having a crevice between a minute primary particle with which it ranked with radiately and said at least a part of minute primary particle was radiately located in a line toward a method of outside from the center of an aggregated particle, and an adjoining minute primary particle similarly radiately located in a line.
[Claim 2]The positive active material for nonaqueous electrolyte secondary cells according to claim 1, wherein at least a part of mutual minute primary particle which constitutes said aggregated particle has joined by sintering.
[Claim 3]that shape of said aggregated particle is spherical, or an ellipse -- the positive active material for nonaqueous electrolyte secondary cells according to claim 1 or 2 characterized by a spherical thing.
[Claim 4]Positive active material for nonaqueous electrolyte secondary cells of claim 1-3, wherein mean particle diameter of said aggregated particle is 30 micrometers or less in not less than 2 micrometers given in any 1 paragraph.
[Claim 5]Positive active material for nonaqueous electrolyte secondary batteries of claim 1-4, wherein mean particle diameter of said primary particle is 10 micrometers or less in 0.4 micrometers or more given in any 1 paragraph.
[Claim 6]A nonaqueous electrolyte secondary cell making positive active material of claim 1-5 given in any 1 paragraph into a component.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention is a thing about the positive active material of the nonaqueous electrolyte secondary cell using the carbon etc. which can carry out occlusion of a lithium metal, a lithium alloy, or the lithium to a negative electrode, It is related with the nonaqueous electrolyte secondary cell using the positive active material for nonaqueous electrolyte secondary cells and this positive active material which improved the service capacity at the time of the heavy load of a cell especially.
[0002]
[Description of the Prior Art]In recent years, development of a rechargeable battery with the high capacity which has small size and a lightweight and high energy density is strongly desired with the spread of portable devices, such as a cellular phone and a notebook sized personal computer. There is a rechargeable lithium-ion battery which uses a lithium metal, a lithium alloy, or carbon as a negative electrode as such a thing, and the present research and development are done briskly. And since 4V class high voltage is obtained, the rechargeable lithium-ion battery which used for positive active material cobalt acid lithium ($LiCoO_2$) in which composition is comparatively easy is expected as a cell with high energy density, and is put in practical use widely.
[0003]However, the amounts of conducting agents, such as raising the tap density of positive active material to the demand of the latest, further high-capacity-izing and high-current-izing and carbon mixed with positive active material, were reduced, and a measure, such as increasing positive active material substantially, has been needed.
[0004]
[Problem(s) to be Solved by the Invention]Usually, lithium salt [, for example like lithium carbonate] whose $LiCoO_2$ is, Carry out specified quantity mixing of a cobalt compound like cobalt carbonate, and calcinate at the temperature up to 600 ** - 1100 **, or For example, (JP,1-304664,A), Or it is obtained by what (JP,9-283144,A) specified quantity mixing is carried out and lithium carbonate and tricobalt tetroxide whose mean particle diameter is 2 micrometers - 25 micrometers are calcinated for at 800 ** - 900 **, and is a thing.
[0005]However, there was a problem of pack density not going up by the conventional $LiCoO_2$, or service capacity and the capacity at the time of a heavy load falling, if the quantity of a conducting agent

is reduced. In order to solve such a problem, much minute crystals of cobalt acid lithium condense. The spherical positive active material for nonaqueous electrolyte secondary cells which is, carries out and consists of an ellipse ball-like aggregated particle is proposed (Poster Abstracts of 9 th International Meeting on Lithium Batteries). II Thur56-1998.

[0006]Although it was an outstanding material with tap density high [the positive active material which surely was described above], and high service capacity at the time of the usual load, the improvement of the service capacity at the time of a heavy load was not yet enough.

[0007]The place which this invention aims at solution of the problem about the above-mentioned conventional positive active material, and is made into the purpose is providing the nonaqueous electrolyte secondary cell using the positive active material for nonaqueous electrolytic solution secondary batteries and this positive active material excellent in the service capacity at the time of a heavy load.

[0008]

[Means for Solving the Problem]As a cause that capacity at the time of a heavy load is insufficient, the primary particles which constitute an aggregated particle join this invention persons of each other densely, and an electrolysis solution does not fully permeate an inside of an aggregated particle at the time of charge discharge, It becomes impossible for a lithium ion to follow in footsteps of current at the time of a heavy load enough as a result, and a point that capacity does not improve is noted, As a result of examining further wholeheartedly a crevice between a size of a primary particle of positive active material, shape and a size of an aggregated particle in which minute primary particles gathered, shape, and a primary particle, etc., by controlling these factors with high capacity. And it finds out that positive active material with good service capacity at the time of a heavy load is obtained, and came to complete this invention.

[0009]Namely, positive active material for nonaqueous electrolyte secondary cells concerning the 1st embodiment of this invention, It consists of an aggregated particle which many minute primary particles of cobalt acid lithium substantially expressed with general formula $LiCoO_2$ condensed, And it is the positive active material for nonaqueous electrolyte secondary cells using cobalt acid lithium whose tap density it has many minute crevices in which an electrolysis solution may permeate this aggregated particle, and is more than 2.2 g/cm^3, It has a crevice between a minute primary particle with which it ranked with radiately and said at least a part of minute primary particle was radiately located in a line toward a method of outside from the center of an aggregated particle, and an adjoining minute primary particle similarly radiately located in a line. and that shape of this aggregated particle is spherical or an ellipse in which it is preferred that at least a part of mutual minute primary particle which constitutes said aggregated particle has joined by sintering -- a spherical thing is preferred. Furthermore, mean particle diameter of said aggregated particle is 30 micrometers or less in not less than 2 micrometers, and, as for mean particle diameter of this primary particle, it is preferred that it is 10 micrometers or less in 0.4 micrometers or more. An effect also with what [same] replaced less than 40 mol % of cobalt with metal other than cobalt can be acquired.

[0010]A nonaqueous electrolyte secondary cell built over the 2nd embodiment of this invention next made a component positive active material concerning said 1st embodiment.

[0011]

[Embodiment of the Invention]According to the positive active material for nonaqueous electrolyte secondary cells concerning this invention, at least a part of primary particle which constitutes the

aggregated particle is radiately located in a line toward the method of outside from the center of an aggregated particle, And since it is constituted so that it may have a crevice between the minute primary particles which adjoin the minute crystals radiately located in a line and which were similarly radiately located in a line, Since an electrolysis solution permeates the inside of an aggregated particle efficiently and the minute primary particle of the positive active material inside an aggregated particle is contacted enough, the discharge characteristic at the time of a heavy load can be made good.

[0012]And the reason for having made mean particle diameter of the minute primary particle into the range of 0.4 micrometer - 10 micrometers in this invention is that the decomposition reaction of an electrolysis solution is promoted and trouble comes out at the safety of a rechargeable battery in less than 0.4 micrometer, and is because the service capacity at the time of a heavy load will fall if it exceeds 10 micrometers on the other hand. Why the mean particle diameter of the aggregated particle was furthermore 2 micrometers - 30 micrometers, It is because problems, like spreading nature is inferior will arise when producing an electrode if the quantity of a conducting agent required in order for less than 2 micrometers not to cover the expenses of tap density and to give conductivity increases and the mean particle diameter of an aggregated particle exceeds 30 micrometers on the other hand.

[0013]Although said minute primary particle itself is a particle, spherical or the thing for which positive active material is formed by an ellipse ball-like aggregated particle which mutual [these] join by sintering in part at least, and is in within the limits whose mean particle diameter is 2 micrometers - 30 micrometers is preferred. The reason which both minute primary particles joined by sintering in part at least and which it was spherical or was made into the ellipse ball-like aggregated particle is because it becomes possible to be able to raise electric conductivity by this, to reduce the quantity of a required conducting agent and to raise pack density.

[0014]the shape of an aggregated particle -- spherical or an ellipse -- tap density more than 2.2 g/cm^3 cannot be obtained, and the reason made spherical is inferior [service capacity], when it is considered as the shape of infinite forms other than these.

[0015]

[Example]This invention is explained in detail with an example and a comparative example below. Since each tap density of the positive active material obtained by the following examples and comparative examples was more than 2.2 g/cm^3, reference is not made especially individually.

[0016][EXAMPLE] The aggregated particle was almost spherical, after mean particle diameter carried out specified quantity mixing of basic cobalt carbonate and lithium carbonate which are 2 micrometers - 30 micrometers, it calcinated at 900 ** among the air for 10 hours, and the aggregated particle of cobalt acid lithium was obtained.

[0017]When a small quantity was sampled out of the obtained particles and the surface of the aggregated particle was observed by 5000 times with the scanning electron microscope (SEM), it had become the almost spherical aggregated particle which many primary particles whose mean particle diameter is 0.4 micrometer - about 5 micrometers condensed. Furthermore, the opening of a large number (0.2 micrometer - about 2 micrometers) as shown in the SEM photograph of drawing 1 was observed in this aggregated particle.

[0018]When the magnification of SEM was increased 15000 times and observed next, it has checked that the part had joined both the primary particles that constitute the aggregated particle by sintering, respectively. And after embedding the aggregated particle of a small amount of cobalt acid lithium at an epoxy resin, the microtome cutting machine which has a diamond cutter cut the aggregated particle, and

the aggregated particle section was exposed. When the exposed section was observed by 2000 times by SEM like the above, the minute primary particle which constitutes the aggregated particle as shown in the SEM photograph of drawing 2 was able to check the organization which has a crevice between the minute primary particles which are radiately located in a line and adjoin, and which were similarly radiately located in a line.

[0019]The electrochemical measuring apparatus of the single particle based on a report (electrochemistry, Vol.65, 954 (1997)) of Uchida and others performed measurement of the service capacity at the time of the heavy load of the obtained cobalt-acid-lithium aggregated particle. If this measuring device is used, aggregated particle independent evaluation will be attained without being influenced by conducting agent, a binder, etc. As shown in drawing 3, using a two divided up and down with glass filter room type cell, said measuring device lays the aggregated particle 1 of cobalt acid lithium on the glass filter 5, and sets a cell to the observation stand of the optical microscope 2. The tip of the micro lead electrode 3 (Pt/Rh small-gage wire 25 micrometers in diameter) attached to the micromanipulator 4 was contacted to the particles 1, checking the aggregated particle 1 with the image of the CCD camera attached to this optical microscope.

[0020]on the other hand -- the electrolysis solution 6 -- 1 M-$LiClO_4$ / ethylene carbonate (EC)-G ethyl carbonate (DEC) (1:1) mixed solution -- the lithium metal was used for the counter electrode 7. This measuring device was performed in the dry box which passed dew point-60 ** dry air in order to prevent mixing of the moisture out of the atmosphere. Using the PONTESHO stat 8 for micro current, at the time of charge, constant current was sent so that the potential of the micro lead electrode 3 to the counter electrode 7 of a lithium metal might be set to 4.3V in 1 hour, and it set it to 1C of the aggregated particle which has measured the current value. Discharge was passed until the potential of the micro lead electrode 3 to the counter electrode 7 was set to 3.0V with the predetermined constant current value, and it made service capacity quantity of electricity which flowed then. On the basis of the current value at the time of charge, if it was 5 times the predetermined current value of this, for example and was it, it was set to 10C etc. [of this] [5C and 10 times]

[0021]And the example of a charge-and-discharge profile of the independent aggregated particle of the positive active material obtained by the example of this invention is shown in drawing 4, and drawing 4 (a) is the example of a charge-and-discharge profile from which the charge 1C, the discharge 10C, and drawing 4 (b) were obtained by the charge 1C and the discharge 20C. According to the example of this invention, also in the heavy load of the discharge 20C, excess voltage is very small and the discharge characteristic was good as drawing 4 showed.

[0022][Comparative example] The aggregated particle was almost spherical, after mean particle diameter heated beforehand basic cobalt carbonate which is 2-30 micrometers in the air in 850 ** and 4 hours, it mixed with lithium carbonate of the specified quantity, it calcinated at 900 ** among the air for 10 hours, and the aggregated particle of cobalt acid lithium was obtained.

[0023]When a small quantity was sampled out of the obtained particles and the surface of the aggregated particle was observed by SEM at 5000 times, it had become the almost spherical aggregated particle which many primary particles whose mean particle diameter is 0.4 micrometer - about 5 micrometers condensed. Furthermore, the opening of a large number (0.2 micrometer - about 2 micrometers) as shown in the SEM photograph of drawing 5 was observed in this aggregated particle.

[0024]When the magnification of SEM was increased 15000 times and observed next, it has checked

that the part had joined both the primary particles that constitute the aggregated particle by sintering, respectively. After embedding further little aggregated particles at an epoxy resin, the microtome cutting machine which has a diamond cutter cut the aggregated particle, and the aggregated particle section was exposed. When the exposed section was observed in SEM like the above at 2500 times, as shown in the SEM photograph of drawing 6, the crevice was accepted between the minute primary particles which constitute the aggregated particle, but a radiate organization like the above mentioned example did not exist.

[0025]The heavy load characteristic of the obtained cobalt-acid-lithium aggregated particle was measured by the same method as an example. Although the charge-and-discharge profile obtained by the charge 1C of the independent aggregated particle of the positive active material obtained by the comparative example and the discharge 10C was shown in drawing 7, very big excess voltage was observed also in discharge of 10C.

[0026]Although the positive active material for nonaqueous electrolyte secondary cells in this invention becomes the real target which used lithium and cobalt as the main ingredients from $LiCoO_2$, The material which replaced a part of Co with other metal for the purpose of the fall of the stability of a crystal, and electrical conductivity or a manufacture price, If the positive active material which specifically replaced less than 40 mol % of Co with one sort or two sorts or more of metal selected from nickel, Mn, aluminum, zetan, Mg, Ca, Ti, Fe, and Sn also takes the gestalt of this invention, the effect of improving the heavy load characteristic is realizable.

[0027]The positive active material for nonaqueous electrolyte secondary cells concerning this invention consists of an almost spherical aggregated particle where many primary particles in the range whose mean particle diameter is 0.4 micrometer - 10 micrometers condense and which is in the range whose mean particle diameter is 2 micrometers - 30 micrometers so that clearly from the above example and comparative example, And at least a part of minute primary particle which constitutes the aggregated particle is radiately located in a line toward the method of outside from the center of an aggregated particle, And since it has a crevice between the minute primary particle radiately located in a line and the adjoining minute primary particle similarly radiately located in a line, in order that an electrolysis solution may permeate the inside of an aggregated particle efficiently and may spread even round all the corners of a primary particle, At the time of a heavy load, it is small, a discharge characteristic is large, and excess voltage acts as Kougami.

[0028]On the other hand, in the structure where how for the primary particle inside an aggregated particle to be located in a line like a comparative example is irregular, or the crevice is intercepted by particles, the big excess voltage at the time of a heavy load was accepted. Although this cause is not certain, when an electrolysis solution permeates an inside, it is considered with having become strong resistance and the excess voltage at the time of a heavy load having become large.

[0029]the aggregated particle of the positive active material for nonaqueous electrolyte secondary cells in this invention from it being [whose mean particle diameter is 4 micrometers - 30 micrometers] spherical (or -- almost -- an ellipse -- spherical) mostly. Tap density is also high, and since it excelled also in the spreading nature at the time of electrode production and the primary particle has sintered the part mutually further, the electrical resistance between primary particles is low, and since an aggregated particle is not crushed when producing an electrode, a primary particle does not drop out of a charge collector. The nonaqueous electrolyte secondary cell produced using this cobalt acid lithium as positive

active material was excellent in the discharge characteristic at the time of a heavy load.

[0030]

[Effect of the Invention]It becomes possible [the rechargeable battery using the positive active material for nonaqueous electrolyte secondary cells and this concerning this invention] to raise service capacity and the heavy load characteristic as stated above, and it becomes possible to provide the nonaqueous electrolyte secondary cell outstanding by this.

[Translation done.]